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Introduction to Nuclear Magnetic Resonance Spectroscopy

Introduction

Nuclear magnetic resonance spectroscopy (NMR) is a widely used and powerful method that takes advantage of the magnetic properties of certain nuclei. The basic principle behind NMR is that some nuclei exist in specific nuclear spin states when exposed to an external magnetic field. NMR observes transitions between these spin states that are specific to the particular nuclei in question, as well as that nuclei's chemical environment. However, this only applies to nuclei whose spin, I, is not equal to 0, so nuclei where I = 0 are ‘invisible’ to NMR spectroscopy. These properties have led to NMR being used to identify molecular structures, monitor reactions, study metabolism in cells, and is used in medicine, biochemistry, physics, industry, and almost every imaginable branch of science.

Theory

The chemical theory that underlies NMR spectroscopy depends on the intrinsic spin of the nucleus involved, described by the quantum number S. Nuclei with a non-zero spin are always associated with a non-zero magnetic moment, as described by [link], where μ is the magnetic moment, S is the spin, and γ is always non-zero. It is this magnetic moment that allows for NMR to be used; therefore nuclei whose quantum spin is zero cannot be measured using NMR. Almost all isotopes that have both an even number of protons and neutrons have no magnetic moment, and cannot be measured using NMR.

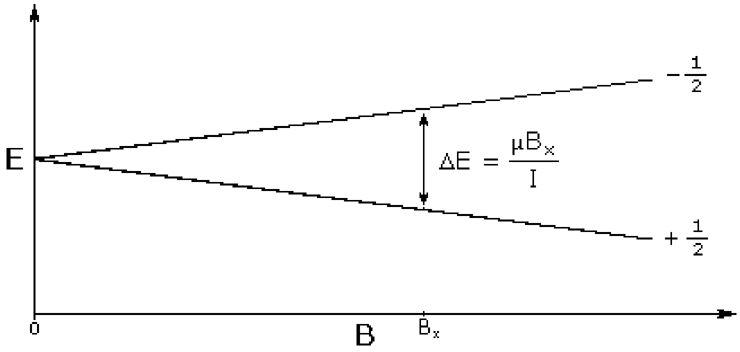
Equation:

$$\mu = \gamma . S$$

In the presence of an external magnetic field (B) for a nuclei with a spin I = $^{1}/_{2}$, there are two spin states present of $+^{1}/_{2}$ and $-^{1}/_{2}$. The difference in energy between these two states at a specific external magnetic field (B_x) are given by [link], and are shown in [link], where E is energy, I is the spin of the nuclei, and μ is the magnetic moment of the specific nuclei being analyzed. The difference in energy shown is always extremely small, so for NMR strong magnetic fields are required to further separate the two energy states. At the applied magnetic fields used for NMR, most magnetic resonance frequencies tend to fall in the radio frequency range.

Equation:

$$E = \mu . B_x / I$$



The difference in energy between two spin states over a varying magnetic field B.

The reason NMR can differentiate between different elements and isotopes is due to the fact that each specific nuclide will only absorb at a very specific frequency. This specificity means that NMR can generally detect one isotope at a time, and this results in different types of NMR: such as ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR, to name only a few.

The subsequent absorbed frequency of any type of nuclei is not always constant, since electrons surrounding a nucleus can result in an effect called nuclear shielding, where the magnetic field at the nucleus is changed (usually lowered) because of the surrounding electron environment. This differentiation of a particular nucleus based upon its electronic (chemical) environment allows NMR be used to identify structure. Since nuclei of the same type in different electron environments will be more or less shielded than another, the difference in their environment (as observed by a difference in the surrounding magnetic field) is defined as the chemical shift.

Instrumentation

An example of an NMR spectrometer is given in [link]. NMR spectroscopy works by varying the machine’s emitted frequency over a small range while the sample is inside a constant magnetic field. Most of the magnets used in NMR machines to create the magnetic field range from 6 to 24 T. The sample is placed within the magnet and surrounded by superconducting coils, and is then subjected to a frequency from the radio wave source. A detector then interprets the results and sends it to the main console.

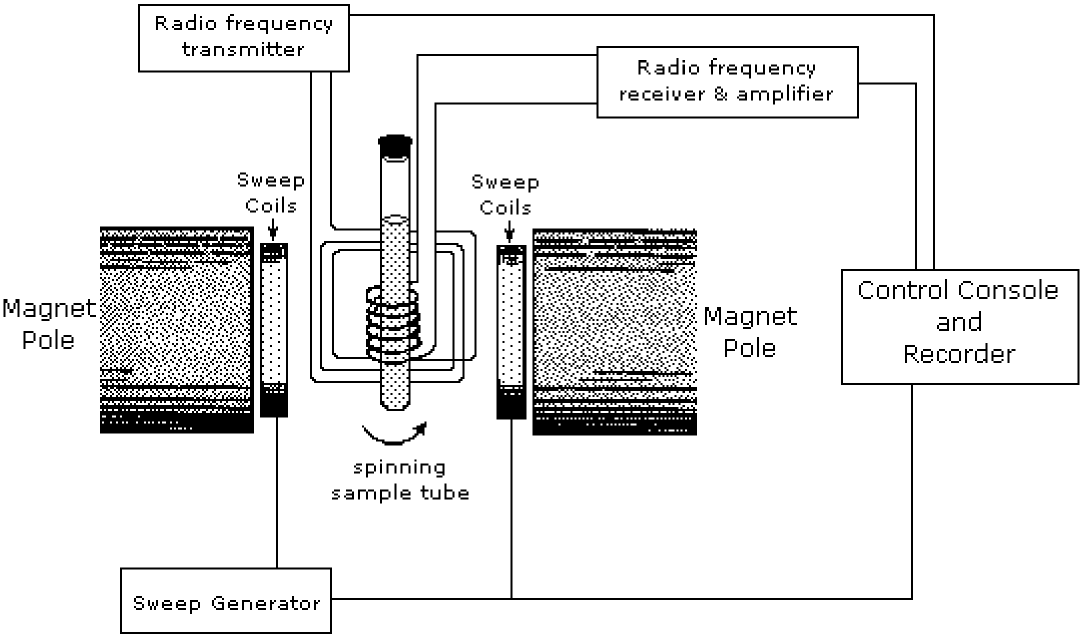

Radio frequency transmitter
Radio frequency receiver & amplifier
Sweep Coils
Sweep Coils
Magnet Pole
Magnet Pole
Control Console and Recorder
spinning sample tube
Sweep Generator

Diagram of an NMR spectrometer.

Interpreting NMR spectra

Chemical shift

The different local chemical environments surrounding any particular nuclei causes them to resonate at slightly different frequencies. This is a result of a nucleus being more or less shielded than another. This is called the chemical shift (δ). One factor that affects chemical shift is the changing of electron density from around a nucleus, such as a bond to an electronegative group. Hydrogen bonding also changes the electron density in ^1H NMR, causing a larger shift. These frequency shifts are miniscule in comparison to the fundamental NMR frequency differences, on a scale of Hz as compared to MHz. For this reason chemical shifts (δ) are described by the unit ppm on an NMR spectra, [link], where H_{ref} = the resonance frequency of the reference, H_{sub} = resonance frequency of the substance, and $H_{machine}$ = operating frequency of the spectometer.

Equation:

$$\delta = \left(\frac{H_{ref} - H_{sub}}{H_{machine}}\right) \times 10^{6}$$

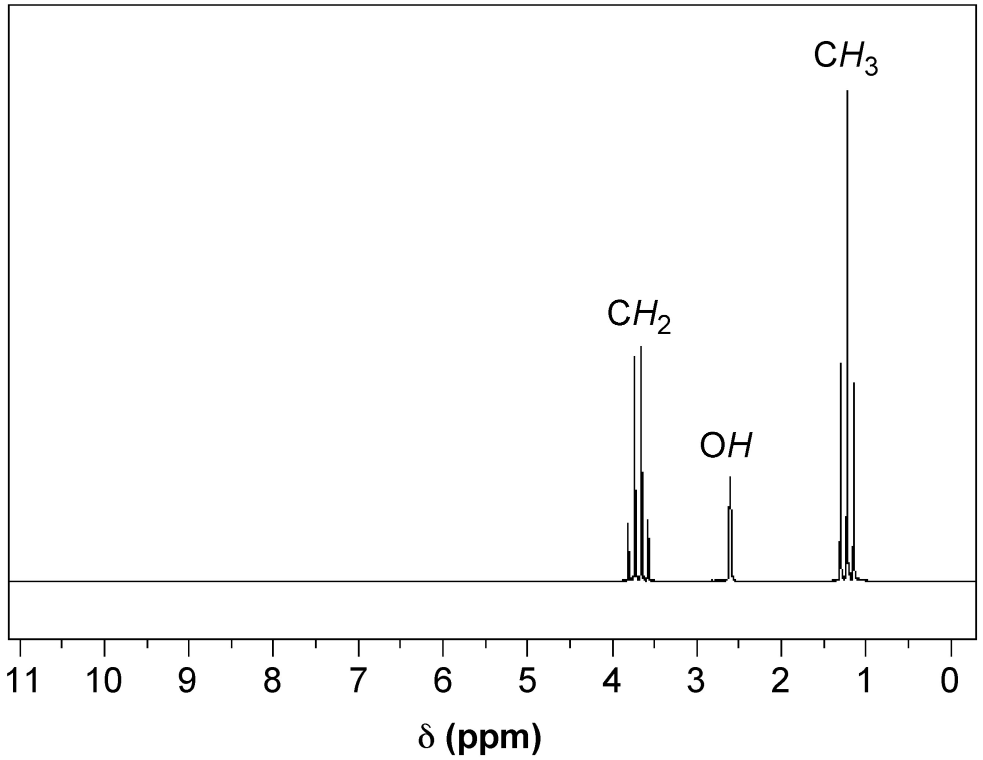
Since the chemical shift (δ in ppm) is reported as a relative difference from some reference frequency, so a reference is required. In ^1H and ^{13}C NMR, for example, tetramethylsilane (TMS, $Si(CH_3)_4$) is used as the reference. Chemical shifts can be used to identify structural properties in a molecule based on our understanding of different chemical environments. Some examples of where different chemical environments fall on a ^1H NMR spectra are given in [link].

Functional group	Chemical shift range (ppm)

Alkyl (e.g., methyl -CH_3)	~ 1
Alkyl adjacent to oxygen (-CH_2-O)	3 - 4
Alkene (=CH_2)	~ 6
Alkyne (C-H)	~ 3
Aromatic	7 - 8

Representative chemical shifts for organic groups in the ^{1}H NMR.

In [link], an ^{1}H NMR spectra of ethanol, we can see a clear example of chemical shift. There are three sets of peaks that represent the six hydrogens of ethanol (C_2H_6O). The presence of three sets of peaks means that there are three different chemical environments that the hydrogens can be found in: the terminal methyl (CH_3) carbon’s three hydrogens, the two hydrogens on the methylene (CH_2) carbon adjacent to the oxygen, and the single hydrogen on the oxygen of the alcohol group (OH). Once we cover spin-spin coupling, we will have the tools available to match these groups of hydrogens to their respective peaks.

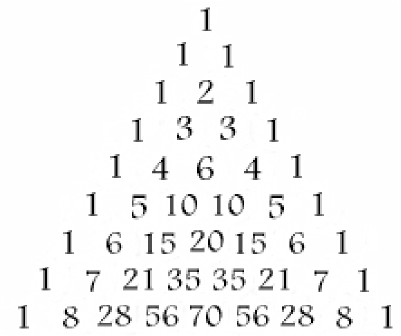


A ^{1}H NMR spectra of ethanol (CH_3CH_2OH).

Spin-spin coupling

Another useful property that allows NMR spectra to give structural information is called spin-spin coupling, which is caused by spin coupling between NMR active nuclei that are not chemically identical. Different spin states interact through chemical bonds in a molecule to give rise to this coupling, which occurs when a nuclei being examined is disturbed or influenced by a nearby nuclear spin. In NMR spectra, this effect is shown through peak splitting that can give direct information concerning the connectivity of atoms in a molecule. Nuclei which share the same chemical shift do not form splitting peaks in an NMR spectra.

In general, neighboring NMR active nuclei three or fewer bonds away lead to this splitting. The splitting is described by the relationship where n neighboring nuclei result in *n*+1 peaks, and the area distribution can be seen in Pascal’s triangle in [link]. However, being adjacent to a strongly electronegative group such as oxygen can prevent spin-spin coupling. For example a doublet would have two peaks with intensity ratios of 1:1, while a quartet would have four peaks of relative intensities 1:3:3:1. The magnitude of the observed spin splitting depends on many factors and is given by the coupling constant *J*, which is in units of Hz.



1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1
1 6 15 20 15 6 1
1 7 21 35 35 21 7 1
1 8 28 56 70 56 28 8 1

Pascal’s triangle.

Referring again to [link], we have a good example of how spin-spin coupling manifests itself in an NMR spectra. In the spectra we have three sets of peaks: a quartet, triplet, and a singlet. If we start with the terminal carbon’s hydrogens in ethanol, using the *n*+1 rule we see that they have two hydrogens within three bonds (i.e., H-C-C-H), leading us to identify the triplet as the peaks for the terminal carbon’s hydrogens. Looking next at the two central hydrogens, they have four NMR active nuclei within three bonds (i.e., H-C-C-H), but there is no quintet on the spectra as might be expected. This can be explained by the fact that the single hydrogen bonded to the oxygen is shielded from spin-spin coupling, so it must be a singlet and the two central hydrogens form the quartet. We have now interpreted the NMR spectra of ethanol by identifying which nuclei correspond to each peak.

Peak intensity

Mainly useful for proton NMR, the size of the peaks in the NMR spectra can give information concerning the number of nuclei that gave rise to that peak. This is done by measuring the peak’s area using integration. Yet even without using integration the size of different peaks can still give relative information about the number of nuclei. For example a singlet associated with three hydrogen atoms would be about 3 times larger than a singlet associated with a single hydrogen atom.

This can also be seen in the example in [link]. If we integrated the area under each peak, we would find that the ratios of the areas of the quartet, singlet, and triplet are approximately 2:1:3, respectively.

Limitations of NMR

Despite all of its upsides, there are several limitations that can make NMR analysis difficult or impossible in certain situations. One such issue is that the desired isotope of an element that is needed for NMR analysis may have little or no natural abundance. For example the natural abundance of ^{13}C, the active isotope for carbon NMR, is about 11%, which works well for analysis. However, in the case of oxygen the active isotope for NMR is ^{17}O, which is only 0.035% naturally abundant. This means that there are certain elements that can essentially never be measured through NMR.

Another problem is that some elements have an extremely low magnetic moment, μ. The sensitivity of NMR machines is based on the magnetic moment of the specific element, but if the magnetic moment is too low it can be very difficult to obtain an NMR spectra with enough peak intensity to properly analyze.

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Basics of Solid-State NMR

Introduction

NMR stands for nuclear magnetic resonance and functions as a powerful tool for chemical characterization. Even though NMR is used mainly for liquids and solutions, technology has progressed to where NMR of solids can be obtained with ease. Aptly named as solid state NMR, the expansion of usable phases has invariably increased our ability to identify chemical compounds. The reason behind difficulties using the solid state lie in the fact that solids are never uniform. When put through a standard NMR, line broadening interactions cannot be removed by rapid molecular motions, which results in unwieldy wide lines which provide little to no useful information. The difference is so staggering that lines broaden by hundreds to thousands of hertz as opposed to less than 0.1 Hz in solution when using an $I = {}^{1}/_{2}$ spin nucleus.

A process known as magic angle spinning (MAS), where the sample is tilted at a specific angle, is used in order to overcome line broadening interactions and achieve usable peak resolutions. In order to understand solid state NMR, its history, operating chemical and mathematical principles, and distinctions from gas phase/solution NMR will be explained.

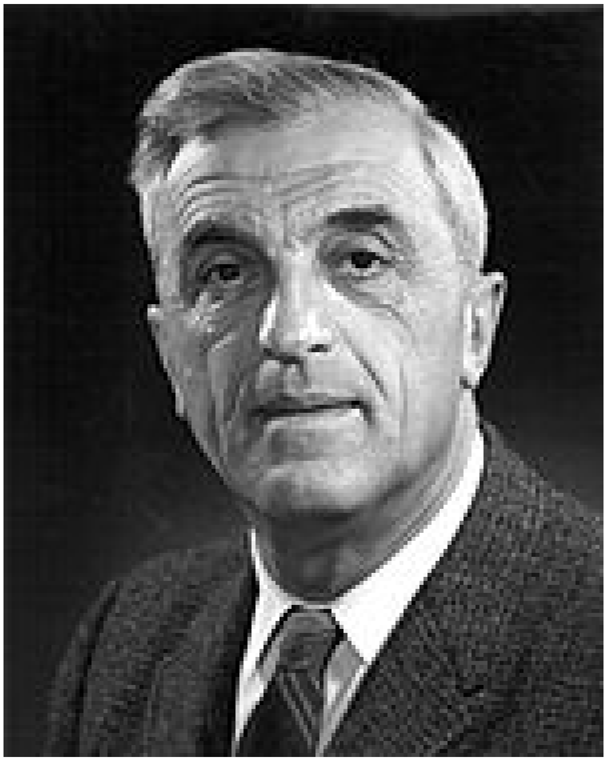
History

The first notable contribution to what we know today as NMR was Wolfgang Pauli's ([link]) prediction of nuclear spin in 1926. In 1932 Otto Stern ([link]) used molecular beams and detected nuclear magnetic moments.

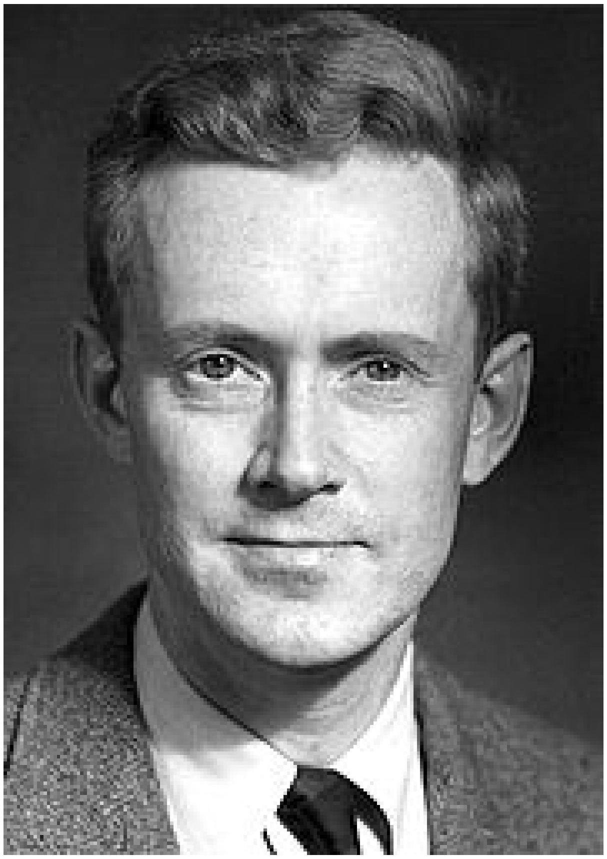
Austrian theoretical physicist Wolfgang Ernst Pauli (1900-1958).

German physicist Otto Stern
(1888 - 1969).

Four years later, Gorter performed the first NMR experiment with lithium fluoride (LiF) and hydrated potassium alum ($K[Al(SO_4)_2]\bullet 12H_2O$) at low temperatures. Unfortunately, he was unable to characterize the molecules and the first successful NMR for a solution of water was taken in 1945 by Felix Bloch ([link]). In the same year, Edward Mills Purcell ([link]) managed the first successful NMR for the solid paraffin. Continuing their research, Bloch obtained the ^1H NMR of ethanol and Purcell obtained that of paraffin in 1949. In the same year, the chemical significance of chemical shifts was discovered. Finally, high resolution solid state NMR was made possible in 1958 by the discovery of magic angle spinning.



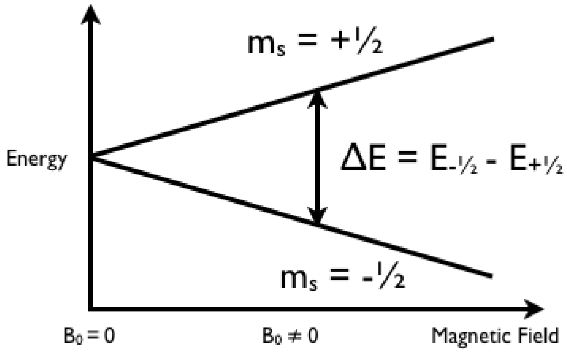
Swiss physicist Felix Bloch (1905-1983).



American physicist Edward Mills Purcell (1912-1997).

How it works: from machine to graph

NMR spectroscopy works by measuring the nuclear shielding, which can also be seen as the electron density, of a particular element. Nuclear shielding is affected by the chemical environment, as different neighboring atoms will have different effects on nuclear shielding, as electronegative atoms will tend to decrease shielding and vice versa. NMR requires the elements analyzed to have a spin state greater than zero. Commonly used elements are ^{1}H, ^{13}C, and ^{29}Si. Once inside the NMR machine, the presence of a magnetic field splits the spin states ([link]).



Spin state splitting as a function of applied magnetic field.

From ([link]) we see that a spin state of $^{1}/_{2}$ is split into two spin states. As spin state value increases, so does the number of spin states. A spin of 1 will have three spin states, $^{3}/_{2}$ will have four spin states, and so on. However, higher spin states increases the difficulty to accurately read NMR results due to confounding peaks and decreased resolution, so spin states of ½ are generally preferred. The E, or radiofrequency shown in ([link]) can be described by [link], where µ is the magnetic moment, a property intrinsic to each particular element. This constant can be derived from [link], where ϒ is the gyromagnetic ratio, another element dependent quantity, h is Planck’s constant, and I is the spin.

Equation:

$$E = \mu B_0 H_0$$

Equation:

$$\mu = \gamma h (I(I+1))^{1/2}$$

[link] can have E substituted for hν, leading to [link], which can solve for the NMR resonance frequency (v).

Equation:

$$h\nu = \mu B_0 H_0$$

Using the frequency (v), the δ, or expected chemical shift may be computed using [link].

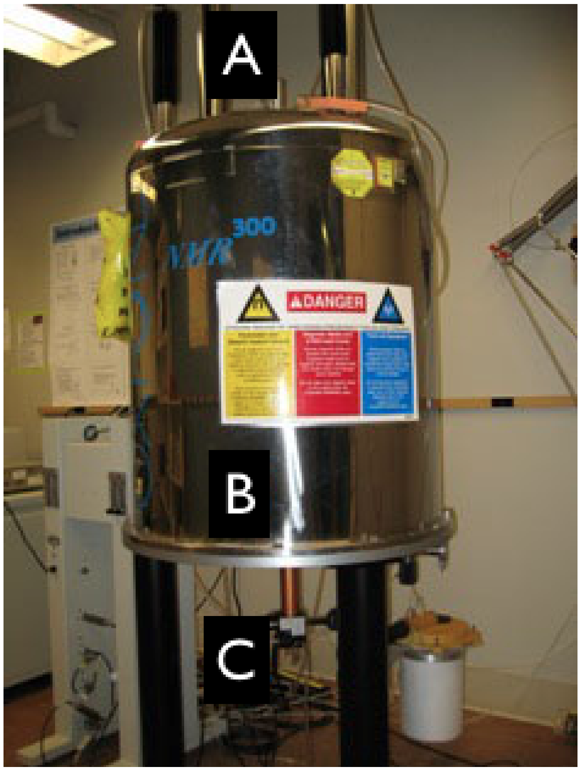
Equation:

$$\delta = \frac{(\nu_{\text{observed}} - \nu_{\text{reference}})}{\nu_{\text{spectrometer}}}$$

Delta (δ) is observed in ppm and gives the distance from a set reference. Delta is directly related to the chemical environment of the particular atom. For a low field, or high delta, an atom is in an environment which produces induces less shielding than in a high field, or low delta.

NMR instrument

An NMR can be divided into three main components: the workstation computer where one operates the NMR instrument, the NMR spectrometer console, and the NMR magnet. A standard sample is inserted through the bore tube and pneumatically lowered into the magnet and NMR probe ([link]).



Standard NMR instrument, with main components labeled: (A) bore tube, (B) outer magnet shell, (C) NMR probe.

The first layer inside the NMR ([link]) is the liquid nitrogen jacket. Normally, this space is filled with liquid nitrogen at 77 K. The liquid nitrogen reservoir space is mostly above the magnet so that it can act as a less expensive refrigerant to block infrared radiation from reaching the liquid helium jacket.

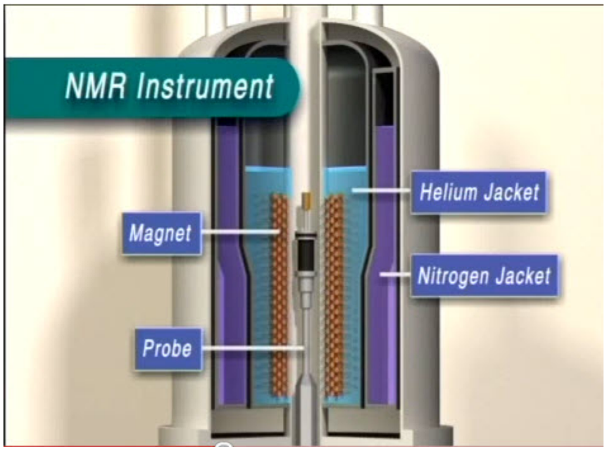


Diagram of the main layers inside an NMR machine.

The layer following the liquid nitrogen jacket is a 20 K radiation shield made of aluminum wrapped with alternating layers of aluminum foil and open weave gauze. Its purpose is to block infrared radiation which the 77 K liquid nitrogen vessel was unable to eliminate, which increases the ability for liquid helium to remain in the liquid phase due to its very low boiling point. The liquid helium vessel itself, the next layer, is made of stainless steel wrapped in a single layer of aluminum foil, acting once again as an infrared radiation shield. It is about 1.6 mm thick and kept at 4.2 K.

Inside the vessel and around the magnet is the aluminum baffle, which acts as another degree of infrared radiation protection as well as a layer of protection for the superconducting magnet from liquid helium reservoir fluctuations, especially during liquid helium refills. The significance is that superconducting magnets at low fields are not fully submerged in liquid helium, but higher field superconducting magnets must maintain the superconducting solenoid fully immersed in liquid helium The vapor above the liquid itself is actually enough to maintain superconductivity of most magnets, but if it reaches a temperature above 10 K, the magnet quenches. During a quench, the solenoid exceeds its critical temperature for superconductivity and becomes resistive, generating heat. This heat, in turn, boils off the liquid helium. Therefore, a small opening at the very base of the baffle exists as a path for the liquid helium to reach the magnet surface so that during refills the magnet is protected from accidental quenching.

Problems with solid state NMR

The most notable difference between solid samples and solution/gas in terms of NMR spectroscopy is that molecules in solution rotate rapidly while those in a solid are fixed in a lattice. Different peak readings will be produced depending on how the molecules are oriented in the magnetic field because chemical shielding depends upon the orientation of a molecule, causing chemical shift anisotropy. Therefore, the effect of chemical shielding also depends upon the orientation of the molecule with respect to the spectrometer. These counteracting forces are balanced out in gases and solutions because of their randomized molecular movement, but become a serious issue with fixed molecules observed in solid samples. If the chemical shielding isn’t determined accurately, neither will the chemical shifts (δ).

Another issue with solid samples are dipolar interactions which can be very large in solid samples causing linewidths of tens to hundreds of kilohertz to be generated. Dipolar interactions are tensor quantities, which demonstrate values dependent on the orientation and placement of a molecule in reference to its surroundings. Once again the issue goes back to the lattice structure of solids, which are in a fixed location. Even though the molecules are fixed, this does not mean that nuclei are evenly spread apart. Closer nuclei display greater dipolar interactions and vice versa, creating the noise seen in spectra of NMR not adapted for solid samples. Dipolar interactions are averaged out in solution states because of randomized movement. Spin state repulsions are averaged out by molecular motion of solutions and gases. However, in solid state, these interactions are not averaged and become a third source of line broadening.

Magic angle spinning

In order to counteract chemical shift anisotropy and dipolar interactions, magic angle spinning was developed. As discussed above, describing dipolar splitting and chemical shift aniostoropy interactions respectively, it becomes evident that both depend on the geometric factor ($3\cos^2\theta-1$).

Equation:

$$\text{Dipolar splitting} = C(\mu_0/8\pi)(\gamma_a\gamma_x/r^2_{ax})(3\cos^2\theta_{iz}-1)$$

Equation:

$$\sigma_{zz} = \bar{\sigma} + {}^1/_3\Sigma\sigma_{ii}(3\cos^2\theta_{iz}-1)$$

If this factor is decreased to 0, then line broadening due to chemical shift anisotropy and dipolar interactions will disappear. Therefore, solid samples are rotated at an angle of 54.74˚, effectively allowing solid samples to behave similarly to solutions/gases in NMR spectroscopy. Standard spinning rates range from 12 kHz to an upper limit of 35 kHz, where higher spin rates are necessary to remove higher intermolecular interactions.

Application of solid state NMR

The development of solid state NMR is a technique necessary to understand and classify compounds that would not work well in solutions, such as powders and complex proteins, or study crystals too small for a different characterization method.

Solid state NMR gives information about local environment of silicon, aluminum, phosphorus, etc. in the structures, and is therefore an important tool in determining structure of molecular sieves. The main issue frequently encountered is that crystals large enough for X-Ray crystallography cannot be grown, so NMR is used since it determines the local environments of these elements. Additionally, by using ^{13}C and ^{15}N, solid state NMR helps study amyloid fibrils, filamentous insoluble protein aggregates related to neurodegenerative diseases such as Alzheimer’s disease, type II diabetes, Huntington’s disease, and prion diseases.

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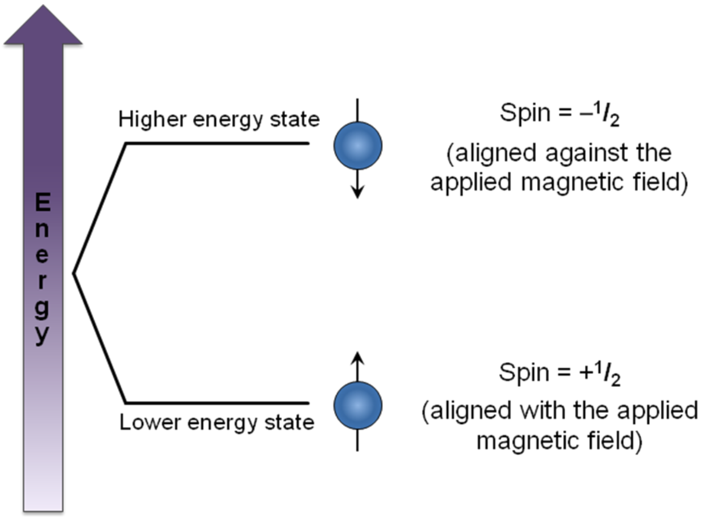
NMR Spin Coupling

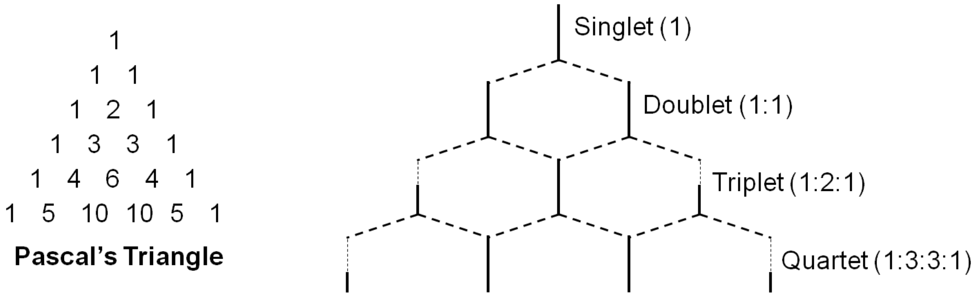
The basis of spin coupling

Nuclear magnetic resonance (NMR) signals arise when nuclei absorb a certain radio frequency and are excited from one spin state to another. The exact frequency of electromagnetic radiation that the nucleus absorbs depends on the magnetic environment around the nucleus. This magnetic environment is controlled mostly by the applied field, but is also affected by the magnetic moments of nearby nuclei. Nuclei can be in one of many spin states ([link]), giving rise to several possible magnetic environments for the observed nucleus to resonate in. This causes the NMR signal for a nucleus to show up as a multiplet rather than a single peak.


Energy
Higher energy state
Spin = –1/2
(aligned against the applied magnetic field)
Lower energy state
Spin = +1/2
(aligned with the applied magnetic field)

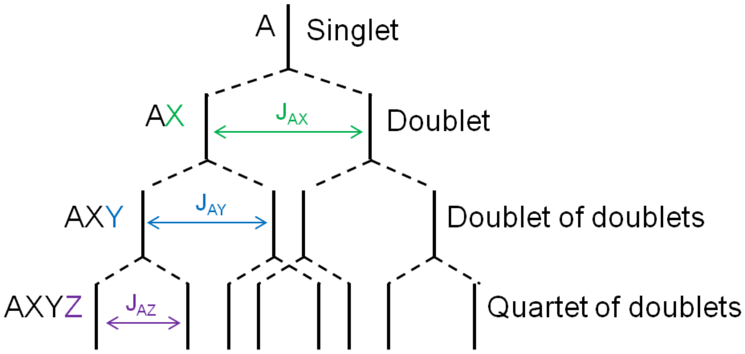
The different spin states of a nucleus (I = $^1/_2$) in a magnetic field. These different states increase or decrease the effective magnetic field experienced by a nearby nucleus, allowing for two distinct signals.

When nuclei have a spin of I = $^1/_2$ (as with protons), they can have two possible magnetic moments and thus split a single expected NMR signal into two signals. When more than one nucleus affects the magnetic environment of the nucleus being examined, complex multiplets form as each nucleus splits the signal into two additional peaks. If those nuclei are magnetically equivalent to each other, then some of the signals overlap to form peaks with different relative intensities. The multiplet pattern can be predicted by Pascal’s triangle ([link]), looking at the n^{th} row, where n = number of nuclei equivalent to each other but *not* equivalent to the one being examined. In this case, the number of peaks in the multiplet is equal to $n + 1$



Pascal’s triangle predicts the number of peaks in a multiplet and their relative intensities.

When there is more than one type of nucleus splitting an NMR signal, then the signal changes from a multiplet to a group of multiplets ([link]). This is caused by the different *coupling constants* associated with different types of nuclei. Each nucleus splits the NMR signal by a different width, so the peaks no longer overlap to form peaks with different relative intensities.



The splitting tree of different types of multiplets.

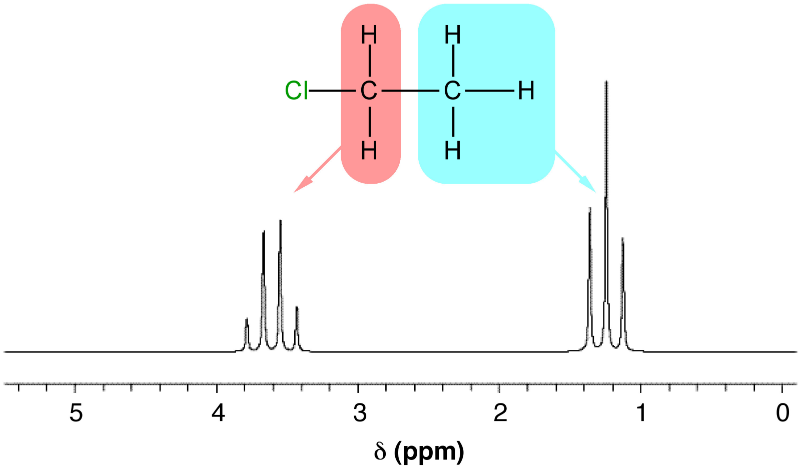
When nuclei have I > $^{1}/_{2}$, they have more than two possible magnetic moments and thus split NMR signals into more than two peaks. The number of peaks expected is 2I + 1, corresponding to the number of possible orientations of the magnetic moment. In reality however, some of these peaks may be obscured due to quadrupolar relaxation. As a result, most NMR focuses on I = $^{1}/_{2}$ nuclei such as ^{1}H, ^{13}C, and ^{31}P.

Multiplets are centered around the chemical shift expected for a nucleus had its signal not been split. The total area of a multiplet corresponds to the number of nuclei resonating at the given frequency.

Spin coupling in molecules

Looking at actual molecules raises questions about which nuclei can cause splitting to occur. First of all, it is important to realize that only nuclei with I ≠ 0 will show up in an NMR spectrum. When I = 0, there is only one possible spin state and obviously the nucleus cannot flip between states. Since the NMR signal is based on the absorption of radio frequency as a nucleus transitions from one spin state to another, I = 0 nuclei do not show up on NMR. In addition, they do not cause splitting of other NMR signals because they only have one possible magnetic moment. This simplifies NMR spectra, in particular of organic and organometallic compounds, greatly, since the majority of carbon atoms are ^{12}C, which have I = 0.

For a nucleus to cause splitting, it must be close enough to the nucleus being observed to affect its magnetic environment. The splitting technically occurs through bonds, not through space, so as a general rule, only nuclei separated by three or fewer bonds can split each other. However, even if a nucleus is close enough to another, it may not cause splitting. For splitting to occur, the nuclei must also be non-equivalent. To see how these factors affect real NMR spectra, consider the spectrum for chloroethane ([link])

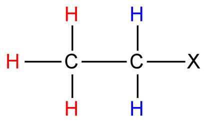
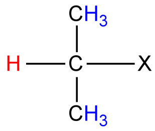
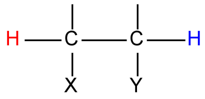
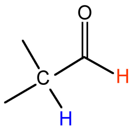


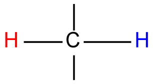
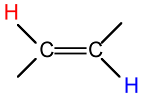
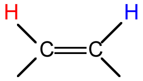
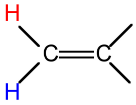
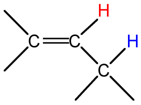
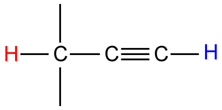
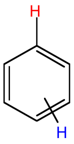
The NMR spectrum for chloroethane. Adapted from A. M. Castillo, L. Patiny, and J. Wist. *J. Magn. Reson.*, 2010, **209**, 123.

Notice that in [link] there are two groups of peaks in the spectrum for chloroethane, a triplet and a quartet. These arise from the two different types of I ≠ 0 nuclei in the molecule, the protons on the methyl and methylene groups. The multiplet corresponding to the CH_3 protons has a relative integration (peak area) of three (one for each proton) and is split by the two methylene protons ($n = 2$), which results in $n + 1$ peaks, i.e., 3 which is a triplet. The multiplet corresponding to the CH_2 protons has an integration of two (one for each proton) and is split by the three methyl protons (($n = 3$) which results in $n + 1$ peaks, i.e., 4 which is a quartet. Each group of nuclei splits the other, so in this way, they are *coupled*.

Coupling constants

The difference (in Hz) between the peaks of a mulitplet is called the *coupling constant*. It is particular to the types of nuclei that give rise to the multiplet, and is independent of the field strength of the NMR instrument used. For this reason, the coupling constant is given in Hz, not ppm. The coupling constant for many common pairs of nuclei are known ([link]), and this can help when interpreting spectra.

Structural type	Coupling constant (Hz)
	6 - 8
	5 - 7
	2 - 12
	0.5 - 3

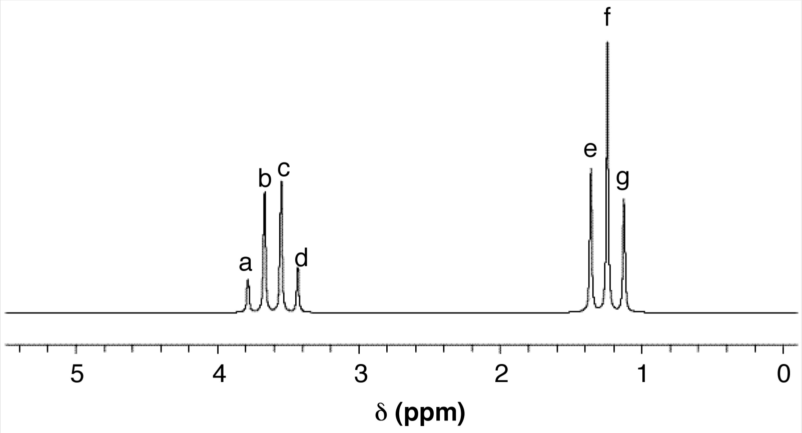
	12 - 15
	12 - 18
	7 - 12
	0.5 - 3
	3 - 11
	2 - 3
	*ortho* = 6 - 9; *meta* = 1 - 3; *para* = 0 - 1

Typical coupling constants for various organic structural types.

Coupling constants are sometimes written ^{n}J to denote the number of bonds (n) between the coupled nuclei. Alternatively, they are written as J(H-H) or J_{HH} to indicate the coupling is between two hydrogen atoms. Thus, a coupling constant between a phosphorous atom and a hydrogen would be written as J(P-H) or J_{PH}. Coupling constants are calculated empirically by measuring the distance between the peaks of a multiplet, and are expressed in Hz.

Example:

Coupling constants may be calculated from spectra using frequency or chemical shift data. Consider the spectrum of chloroethane shown in [link] and the frequency of the peaks (collected on a 60 MHz spectrometer) given in [link].



^{1}H NMR spectrum of chloroethane. Peak positions for labeled peaks are given in [link].

Peak label	δ (ppm)	ν (Hz)

a	3.7805	226.83
b	3.6628	219.77
c	3.5452	212.71
d	3.4275	205.65
e	1.3646	81.88
f	1.2470	74.82
g	1.1293	67.76

Chemical shift in ppm and Hz for all peaks in the ^{1}H NMR spectrum of chloroethane. Peak labels are given in [link].

To determine the coupling constant for a multiplet (in this case, the quartet in [link]), the difference in frequency (ν) between each peak is calculated and the average of this value provides the coupling constant in Hz. For example using the data from [link]:
Frequency of peak c - frequency of peak d = 212.71 Hz – 205.65 Hz = 7.06 Hz
Frequency of peak b - frequency of peak c = 219.77 Hz – 212.71 Hz = 7.06 Hz
Frequency of peak a - frequency of peak b = 226.83 Hz – 219.77 Hz = 7.06 Hz
Average: 7.06 Hz
∴ J(H-H) = 7.06 Hz

Note: In this case the difference in frequency between each set of peaks is the same and therefore an average determination is not strictly necessary. In fact for 1st order spectra they should be the same. However, in some cases the peak picking programs used will result in small variations, and thus it is necessary to take the trouble to calculate a true average.

To determine the coupling constant of the same multiplet using chemical shift data (δ), calculate the difference in ppm between each peak and average the values. Then multiply the chemical shift by the spectrometer field strength (in this case 60 MHz), in order to convert the value from ppm to Hz:
Chemical shift of peak c - chemical shift of peak d = 3.5452 ppm – 3.4275 ppm = 0.1177 ppm
Chemical shift of peak b - chemical shift of peak c = 3.6628 ppm – 3.5452 ppm = 0.1176 ppm
Chemical shift of peak a - chemical shift of peak b = 3.7805 ppm – 3.6628 ppm = 0.1177 ppm
Average: 0.1176 ppm
Average difference in ppm x frequency of the NMR spectrometer = 0.1176 ppm x 60 MHz = 7.056 Hz
∴ *J*(H-H) = 7.06 Hz

Exercise:

Problem:

Calculate the coupling constant for triplet in the spectrum for chloroethane ([link]) using the data from [link].

Solution:

Using frequency data:
Frequency of peak f - frequency of peak g = 74.82 Hz – 67.76 Hz = 7.06 Hz
Frequency of peak e - frequency of peak f = 81.88 Hz – 74.82 Hz = 7.06 Hz
Average = 7.06 Hz
∴ *J*(H-H) = 7.06 Hz

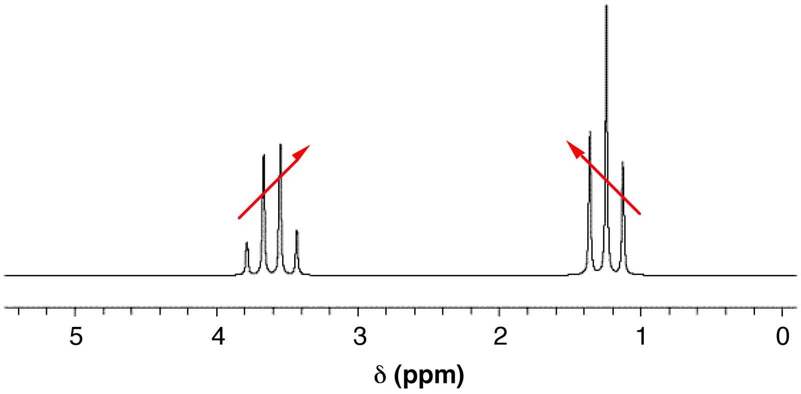
Alternatively, using chemical shift data:
Chemical shift of peak f - chemical shift of peak g = 1.2470 ppm – 1.1293 ppm = 0.1177 ppm

Chemical shift of peak e - chemical shift of peak f = 1.3646 ppm – 1.2470 ppm = 0.1176 ppm
Average = 0.11765 ppm
0.11765 ppm x 60 MHz = 7.059 Hz
∴ *J*(H-H) = 7.06 Hz

Notice the coupling constant for this multiplet is the same as that in the example. This is to be expected since the two multiplets are coupled with each other.

Second-order coupling

When coupled nuclei have similar chemical shifts (more specifically, when Δν is similar in magnitude to *J*), *second-order coupling* or *strong coupling* can occur. In its most basic form, second-order coupling results in “roofing” ([link]). The coupled multiplets point to or lean toward each other, and the effect becomes more noticeable as Δν decreases. The multiplets also become off-centered with second-order coupling. The midpoint between the peaks no longer corresponds exactly to the chemical shift.



Roofing can be seen in the NMR spectrum of chloroethane. Adapted from A. M. Castillo, L. Patiny, and J. Wist, *J. Magn. Reson.*, 2010, **209**, 123.

In more drastic cases of strong coupling (when $\Delta\nu \approx J$), multiplets can merge to create deceptively simple patterns. Or, if more than two spins are involved, entirely new peaks can appear, making it difficult to interpret the spectrum manually. Second-order coupling can often be converted into first-order coupling by using a spectrometer with a higher field strength. This works by altering the $\Delta\nu$ (which is dependent on the field strength), while J (which is independent of the field strength) stays the same.

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NMR

Experiment 1 NMR (Nuclear Magnetic Resonance Spectroscopy

Objective

To introduce or re-acquaint you to the fundamentals of Nuclear Magnetic Resonance spectroscopy (NMR spectroscopy) and to show you how the information obtained from this technique can be used to determine molecular composition and structure. Mass (MS), infrared (IR), and nuclear magnetic resonance (NMR) spectrums (^1H and ^{13}C) are useful tools for analyzing unknown organic compounds.

Grading

- The correctness and thoroughness of your observations.
- The ability to deduce the chemical structure from the NMR spectra.
- Completion of Laboratory Revision Questions and Report Questions.

Background Information

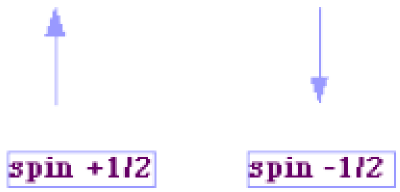
Nuclear Magnetic Resonance (NMR) spectroscopy is an analytical technique based upon the nuclear properties of some types of atoms. Many atoms have isotopes which possess a nuclear magnetic moment, just as the electron does, having a spin of 1/2. Atomic nuclei may have no spin, spin of 1/2, or other spins which are increments of 1/2 (1, 2, etc.). For organic chemists, the most useful nuclei for observation are usually those with spin 1/2. Nuclei with other spins may be studied, but their signals are sometimes observed only under special circumstances and will not be discussed here.
A number of nuclei have spin 1/2 and are very useful for study by NMR spectroscopy. Table 1 lists a number of these elements and their natural abundances. ^1H, ^{13}C, ^{31}P, ^{19}F, and ^{15}N are of particular interest to organic chemists.

Table 1. Common Nuclei with Spin 1/2

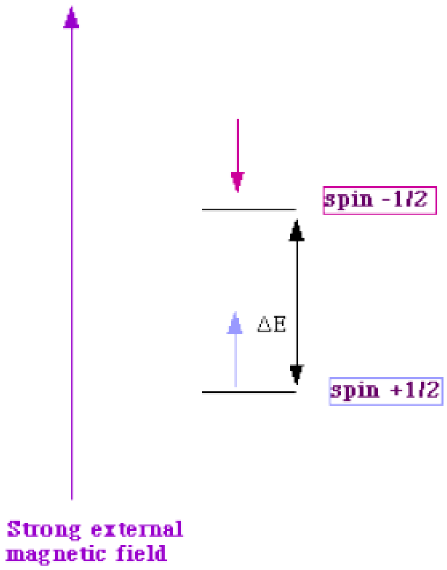
Nucleus	Natural Abundance (%)
^{1}H	99.985
^{13}C	1.11
^{31}P	100.0
^{15}N	0.37
^{19}F	100.0
$^{103}\mathrm{Rh}$	100.0
$^{107}\mathrm{Ag}$	51.8
$^{109}\mathrm{Ag}$	48.2
$^{117}\mathrm{Sn}$	7.7
$^{119}\mathrm{Sn}$	8.6
$^{77}\mathrm{Se}$	7.6
$^{125}\mathrm{Te}$	7.0
$^{195}\mathrm{Pt}$	33.8
$^{203}\mathrm{Tl}$	29.5
$^{205}\mathrm{Tl}$	70.5
$^{207}\mathrm{Pb}$	22.1

In the absence of an external magnetic field, nuclei with a spin of 1/2 have two possible spin states that are equal in energy. These are labeled +1/2 and

-1/2.



If we place the nuclei in a strong external magnetic field, these energy levels are no longer equal.



If we then apply a magnetic field that corresponds in energy to the separation energy (ΔE), the molecule will absorb that energy and cause the nucleus to go from the parallel spin state to the anti-parallel spin state. The energy that is applied to cause this change in spin state is in the radiofrequency range of the electromagnetic spectrum.

Most commonly a sample solution is prepared and placed in a glass tube that is very uniform and has thin walls. The sample is then placed inside a high field magnet. In older instruments, a variable Rf frequency was applied to the sample to sweep out a range of radiofrequencies, thereby generating a spectrum of the radiofrequency energy absorbed. In newer instruments, a short pulse of radiofrequency energy is used that excites nuclei over a range of frequencies, and the response of all of these nuclei is measured all at once. The spectrum is then obtained by a mathematical transformation of the total signal using the Fourier Transform technique. This is known as FT-

NMR. NMR spectra may also be obtained on solid samples, but the technical difficulties are much greater and will not be covered here.

Because many solvents also have protons present, their use in obtaining NMR spectra is problematic. The signal due to the protons in a typical organic solvent would be so large that it would swamp any signal due to the sample you want to measure - sort of like trying to see a tiny flashlight in broad daylight outdoors. In order to remedy this problem, one could choose solvents which do not have protons such as $\mathrm{CS_2}$ or $\mathrm{CCl_4}$; however, these are not suitable solvents for modern FT spectrometers. A better solution is to use solvents in which the protons have been replaced by deuterium. Such solvents, known as deuterated solvents, have very similar properties to their proton-analogues. Thus deuterated benzene is very similar to normal benzene. While deuterium does have a spin (spin = 1), the frequency at which the deuterium nucleus resonates in a magnetic field is sufficiently different from that of protons so that its presence does not interfere with the detection of proton signals. In reality, not all protons of a solvent are replaced in deuterated solvents such that a residual peak due to the presence of a small quantity of protons can usually be observed. This peak usually serves as a good reference point for determining the chemical shifts of peaks in the sample since the peak locations of common deuterated solvents are well known. One can also add a small amount of TMS [tetramethylsilene, $\mathrm{Si(CH_3)_4}$] to the sample and use its peak to serve as a reference peak as well.

Table 2. Some commonly used deuterated solvents.

d-chloroform	$\mathrm{CDCl_3}$
d_6-benzene	C_6D_6
d_3-acetonitrile	$\mathrm{CD_3CN}$

d_6-acetone	$\mathrm{CD_3}C(=O)\mathrm{CD_3}$
d_4-methanol	$\mathrm{CD_3OD}$
d_8-toluene	$C_6D_5\mathrm{CD_3}$
d_2-dichloromethane	$\mathrm{CD_2Cl_2}$
deuterated water	D_2O

In order to obtain really high field strengths, special magnets have been built of materials that are kept at liquid helium temperatures such that they become superconducting. Typically field strengths of 200, 300, 400, and 500 MHz are commonly employed. Instruments are even being built with field strengths as high as 900 MHz!!! The choice of field strength depends upon the sample and bigger is usually, but not always, better.

Because the field strengths are so high, it is potentially dangerous for persons with pacemakers to enter into the fringe field region of these magnets. The magnets will also erase the magnetic information stored on IDs and credit cards. The stronger magnets have been known to pull heavy tools up into them if someone with tools walks too close to the magnet. This often causes severe damage to the magnet.

In this set of exercises, we are going to concentrate on ^1H NMR spectroscopy since it is the most widely used and simplest of the NMR-active nuclei to discuss.

Chemical Shift

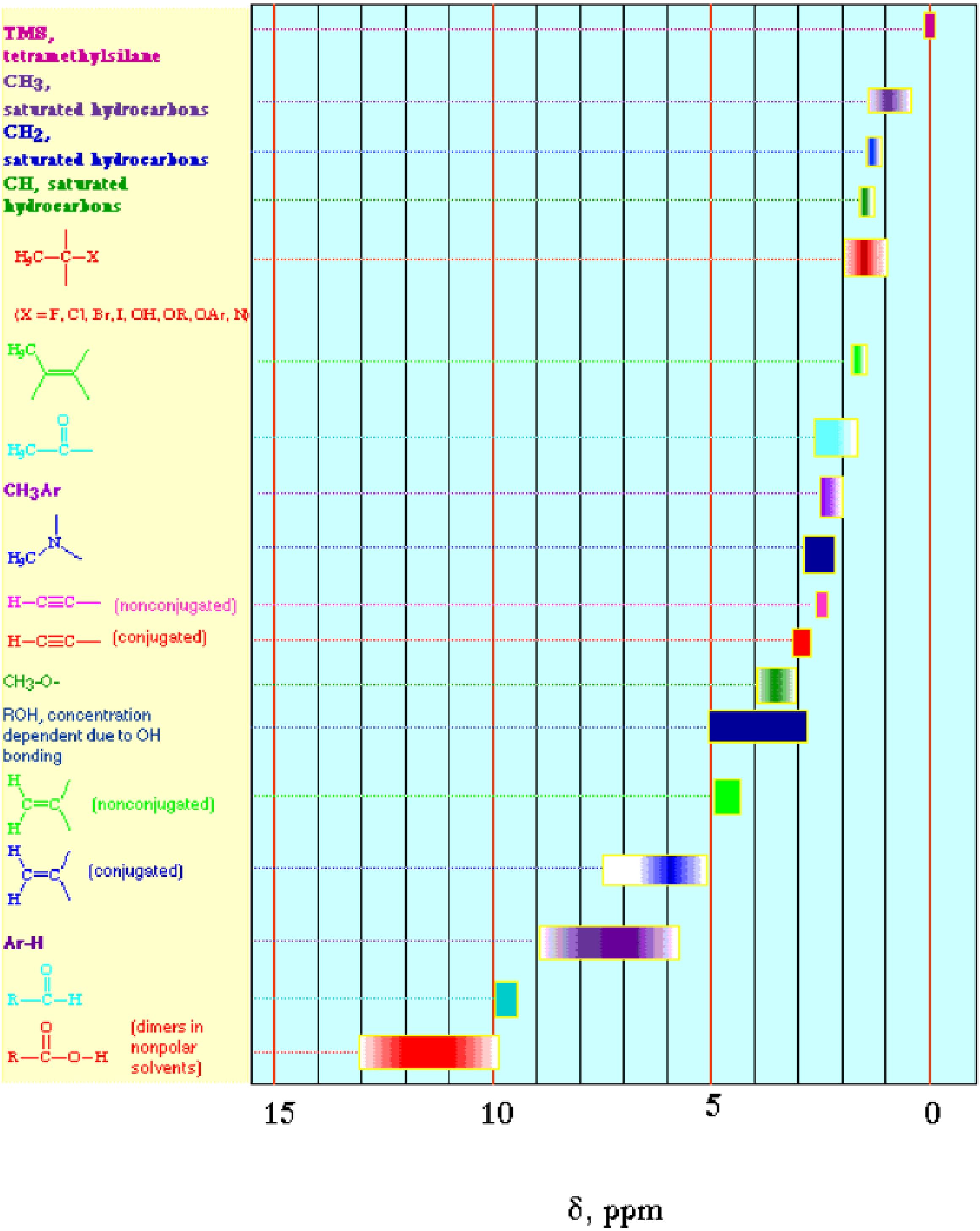
Since the effect being measured involves the measurement of spin states of a nucleus, the values of ΔE will be affected by the local magnetic field of a nucleus being examined.

The local magnetic field is, in turn, affected by the chemical environment of the nucleus. ΔE thus becomes a measure of the chemical environment of the nucleus. Hydrogen atoms bonded to sp^3 carbon atoms are found in different regions of the NMR spectrum from hydrogen atoms attached to alkene sp^2 carbon atoms, alkyne sp carbon atoms, and aromatic sp^2 carbon atoms, oxygen, nitrogen, metals, etc.

We can then use ΔE to give us some information about the nature of the atoms to which a particular hydrogen atom is attached.

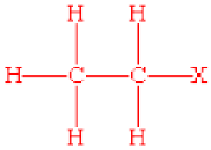
The position of a signal in the NMR spectrum is known as its chemical shift. It has become conventional to reference the NMR signals for hydrogen atoms to the signal found for TMS (tetramethylsilane, $\mathrm{Si(CH_3)_4}$), which has been assigned a value of 0. This scale gives the chemical shifts for other atoms in terms of δ which has frequency units of parts per million (ppm). These values are constant regardless of the field strength of the magnet being used. Most hydrogen atoms attached to organic molecules will resonate in the region δ = 0 to 10 ppm. Often, the more acidic the proton is, the more positive this value becomes (acid protons in carboxylic acids will often be seen at >+10 ppm). This means that the proton is experiencing less electron density around it, a phenomenon known as deshielding. The less electron density there is about a given hydrogen atom, the more deshielded it is. On the opposite extreme, the more electron density a hydrogen atom experiences, the more shielded it is. While most hydrogen atoms are found in the NMR spectra at positive δ values, some may be found at negative δ values. This often occurs when protons are attached to metals (metal hydrides). In these cases, it is typical to find hydrogen signals with δ = 0 to -30 ppm. Chart 1 gives a general guideline for where certain types of protons are found in NMR spectra.

Chart 1. NMR Chemical Shift Assignments



Integration

One of the most useful aspects of NMR spectroscopy is that the signal intensities are directly proportional to the amount of a particular type of H atom present. This can be used in two ways.



First, it can be tell us the number of hydrogen atoms of a given type in relation to other hydrogen atoms present in the molecule. In order to make use of this information, we need to realize that symmetrically equivalent H atoms will have identical chemical shifts.

Thus, if we have an ethyl group, there are three protons from the methyl (CH_3) group and two protons from the methylene (CH_2) group. We expect to see two signals - one for the methyl and one for the methylene - with relative peak areas of 3:2. The process of determining the peak areas is known as integration and the resultant peak areas are known as the integral of the spectrum.

In order to use this information, you need to determine what types of atoms are the same and what types are different within a molecule. Atoms may appear the same for two reasons.

1. One is that they are related by symmetry. That means that the molecule has some symmetry element such as a mirror plane, rotation axis, inversion center, etc. that will make the atoms equivalent.
2. The other possibility is that there is some molecular motion which causes the atoms to adopt an averaged environment. For example, in the ethyl group above, we can draw a static structure which makes the H atoms on the CH_3 group unequal because their proximity to the X group would be different. However, there is free rotation about the C-C bond, so all of the H atoms are whizzing around at very fast speeds, resulting in an averaged environment. There is only one signal observed for this methyl group.

We can also use integration to find the relative amounts of substances present. For example, if we have a mixture of iodomethane and chloromethane dissolved in solution, the ratio of the two peak areas will give the relative amounts of these two compounds. This is useful for determining purity and product yield. We can introduce a known amount of one sample and use its concentration to determine the concentration of another species in solution. The one caution here is that the relative peak areas need to be normalized for the number of protons that produce the signal. In the example of iodomethane and chloromethane, this is easy since they both have methyl groups and the signals are both due to three protons. However, if we were to determine the concentration of dichloromethane versus chloromethane, we would need to take into account that one molecule has three H atoms whereas the other only has two.

$CH_3\text{—}CH_2\text{—}CH_2\text{—}CH_3$

Examples:

Butane

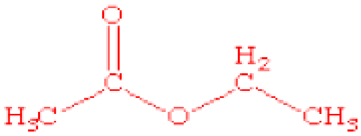
$CH_3\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_3$

The two methyl groups are equivalent to each other, as are the two methylene groups. We would expect to see two signals in a 6:4 or 3:2 ratio.

Pentane

The two methyl groups are equivalent to each other, as are two of the two methylene groups. The middle methylene group is unique. In principle, we would expect to see three signals in a 6:4:2 or 3:2:1 ratio.

Ethyl acetate

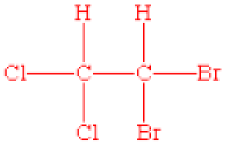


Ethyl acetate has three types of H atoms. There are two methyl groups and one methylene group. We would expect to see three signals in a 3:3:2 area ratio.

Coupling

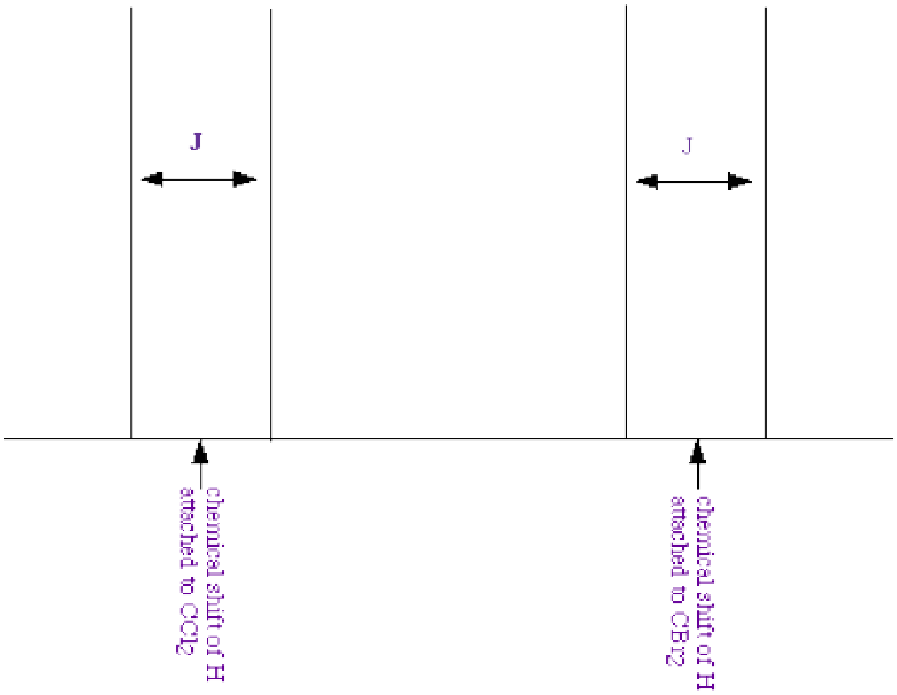
Coupling is another very important aspect of NMR spectroscopy that gives a great deal of information about structure. Coupling results in a signal being split into more signals due to neighboring atoms which also have a nuclear spin. This arises frequently between protons on adjacent carbon atoms. One important aspect of this phenomenon is that equivalent nuclei do not couple to each other.

The reason coupling occurs can be described as follows. For example, let us consider the case of a molecule containing two carbon atoms, each with a single proton and other atoms which do not have a nuclear spin coupling to the protons. One such molecule is 1,1-dibromo-2,2-dichloroethane.



The protons in this molecule are not equivalent, so we would expect to see two signals. Additionally, the proton attached to the CCl_2 group will have two different spin states, +1/2 and -1/2. This means that the proton on the CBr_2 group will see two slightly different magnetic fields depending upon whether the proton on the CCl_2 group is in the +1/2 or -1/2 spin state. Since these spin states are not equivalent in the presence of a large external magnetic field, we actually observe two signals for the H atom attached to the CBr_2 group. This is also true for the hydrogen atom attached to the

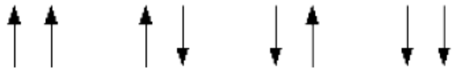
CCl_2 group. In these situations, we say that the proton on the CCl_2 is coupled to the proton on the CBr_2 group. When a peak is split into two equal components by coupling, it is called a doublet. We would expect the proton NMR spectrum of 1,1-dibromo-2,2-dichloroethane to look something like this:


J
J
chemical shift of H attached to CCl2
chemical shift of H attached to CBr2

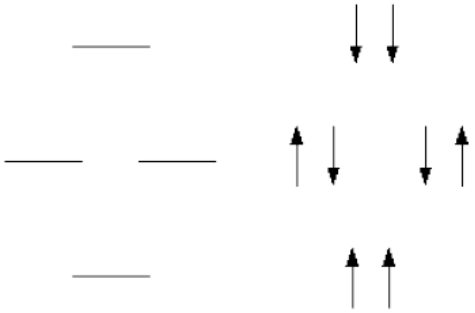
The differences in chemical shift labeled J are known as the coupling constant. If two nuclei are coupled to each other, the coupling constants will be the same. For example, in the case of 1,1-dibromo-2,2-dichloroethane, the two peaks that make up the doublet due to the CCl_2 will be exactly split the same distance as the two peaks that make up the doublet due to the CBr_2 group. In a complex spectrum, this allows us to identify which peaks are coupled to each other. Peaks that are coupled to each other will most likely arise because the H atoms are on adjacent (or nearby) carbon atoms.

We need to consider a couple of other cases in order to have enough information on coupling patterns to understand common problems. There are cases where there is more than one proton on adjacent carbon atoms.

Let us first consider the case where one or more protons on one carbon atom (let's call it Carbon A) "see" two identical protons on a neighboring carbon atom (called Carbon B). What types of magnetic fields will be seen by the protons on Carbon A? To sort this out, we need to consider the different possible spin combinations of the protons on Carbon B. This is done purely by probability. There are four possibilities:

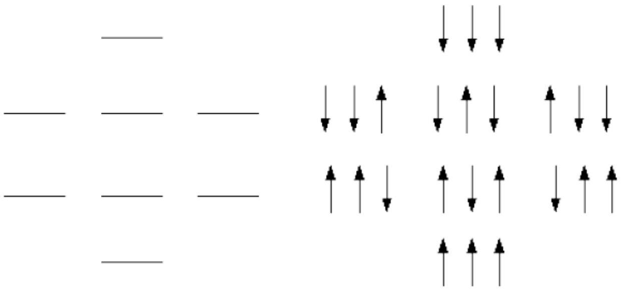


These can be described by the spin numbers: (+1/2, +1/2), (+1/2, -1/2), (-1/2, +1/2), (-1/2, -1/2). It should be easy to see that the energies of the two combinations (+1/2, -1/2) and (-1/2, +1/2) will be equal. We can order these possibilities according to their expected energies in the presence of a strong external field:



The splitting of the protons on Carbon A will be into three signals in a 1:2:1 ratio, the 2 arising because that energy level is twice as probable.

The case for three protons on an adjacent carbon atom is worked out in a similar fashion. Again, the splitting seen by the protons on Carbon A attached to Carbon B (a methyl group) would be as follows:



There are 8 possible combinations of spin states which divide into a 1:3:3:1 ratio. Either all spins are up, two up and one down, two down and one up, or all up. A proton or protons on one carbon atom adjacent to a methyl group will, therefore, split into a quartet with area ratios of 1:3:3:1.

Ethyl

If we have a $CH_3CH_2^-$ group, as in chloroethane, we would expect to see two peaks in a ratio of 3:2. The methyl group signal will be split into a triplet (with relative areas of 1:2:1) by coupling to the methylene protons. The methylene protons are split into a quartet (with relative areas of 1:3:3:1) by coupling to the methyl protons. Therefore, we expect the spectrum of an ethyl group to look something like…

SORRY, THIS MEDIA TYPE IS NOT SUPPORTED.

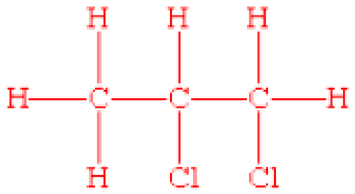
Notice that the chemical shift of a peak split by coupling is defined as the center of the peak pattern. As mentioned earlier, the distance between the peaks of the CH_3 group (the coupling constant) will be the same as the distance between the peaks of the CH_2 group. Also note that the total intensity of the peaks due to the CH_3 group is 1.5 times the size of the total intensity for the peaks of the CH_2 group.

Butane

In the molecule $CH_3CH_2CH_2CH_3$, the methyl groups are equivalent and the methylene groups are equivalent. As described earlier, we would expect to see two signals in a 3:2 ratio. If we now consider coupling, we see that the methyl groups are attached to methylene groups. The CH_3 protons will thus be split into triplets by the methylene protons. Likewise, the methylene protons will be split into quartets by the protons on the methyl groups. However, notice that because the methylene groups are equivalent, they do not couple to each other. Therefore, we expect to see the same pattern as that predicted for the ethyl group shown above.

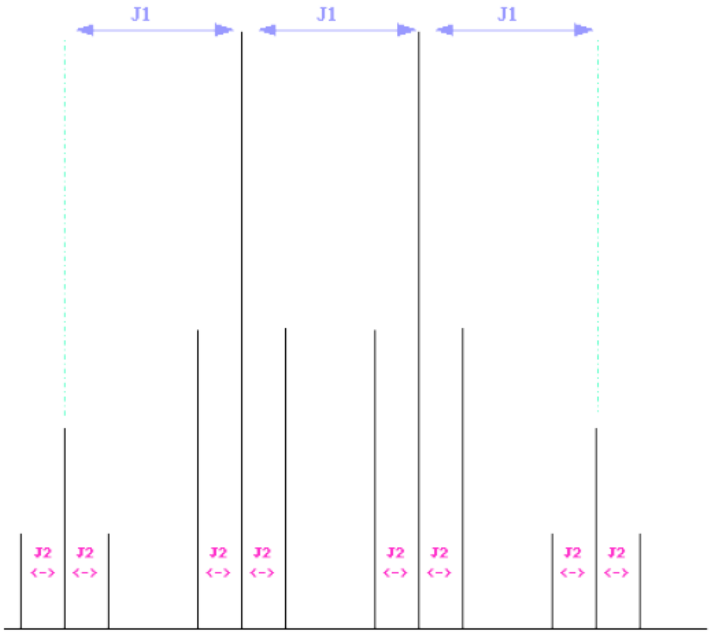
More Complex Coupling Patterns

If a hydrogen atom is attached to a carbon atom to which nonequivalent carbon atoms with different numbers of protons are attached, then a more complex pattern is observed. One arrives at the total number of signals expected by multiplying the individual couplings. For example, consider 1,2-dichloropropane with three carbon atoms having different protons attached:

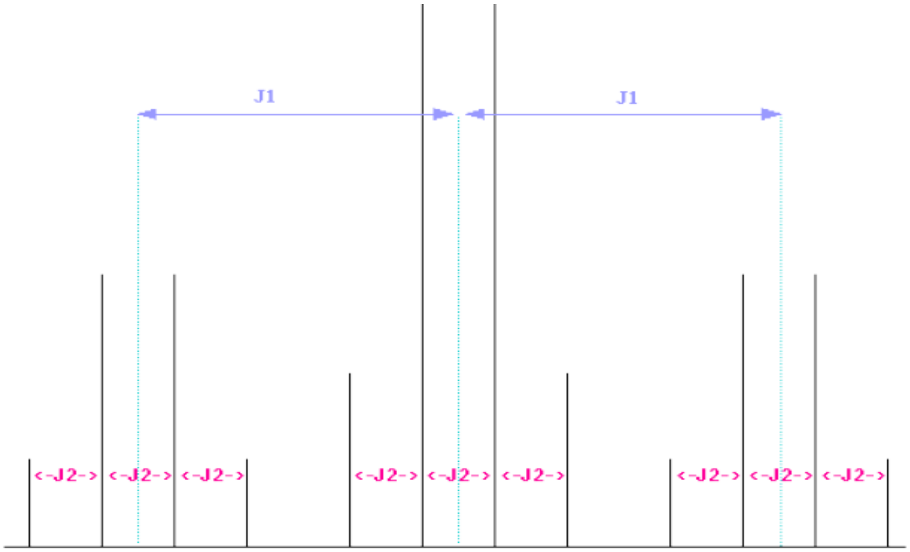


The CH_3 protons will see one adjacent proton and the signal will be split into a doublet. The CH_2 group will likewise be split into a doublet by the CH proton. Coupling between the CH_3 group and the CH_2 group will generally not be observed. However, the CH group in the middle is adjacent to two different types of carbon atoms with different numbers of protons attached. This CH group will be split into a quartet by the CH_3 group and into a triplet by the CH_2 group. The overall pattern will have 4 x 3 lines, or a total of 12, if our instrument is able to resolve all the lines. This pattern would be described as either a triplet of quartets or a quartet of a triplet, depending upon which coupling constant is larger. Often, these complex patterns are not cleanly resolved and a very complex spectrum results. The two limiting possibilities for the CH group would look something like the following. Notice that there are two different coupling constants in each case.

Quartet of triplets



Triplet of quartets



Experimental

You will be given a packet of several spectra. Using the chart and the information on chemical shifts, coupling patterns, and integrated intensities given above as a guide, identify the unknown organic compounds. Answer some review questions to refresh your mind. We will work on number 2 and 5 with you.

Lab Revision Questions: NM

(Total 20 Points)

On my honor, in preparing this report, I know that I am free to use references and consult with others. However, I cannot copy from other students' work or misrepresent my own data.

……………………………………………………….. (signature)

Print Name: ____

1. The atomic weight of Br is listed as 79.909 on the periodic table, but we use 79, not 80, when calculating the molecular weights of Br-containing compounds for mass spectrometry – why? (2 points)

2.

(a) Draw trans-3-bromo-1-butylcyclohexane in planar form (no chair). Be sure to indicate the stereochemistry in your drawing. (2 points)

(b) Now draw both chair conformations of trans-3-bromo-1-butylcyclohexane. (2 points)

(c) Circle the conformer above that is lower in energy. (1 point)

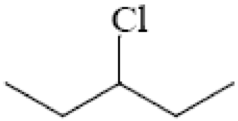
3.

(a) How many degrees of unsaturation does C_5H_7ClO have? (2 points)

(b) Draw an isomer of C_5H_7ClO that contains a ketone (There are many correct answers.). (2 points)

(c) Draw an isomer of C_5H_7ClO that does not contain a ketone. (Again, there are many correct answers.). (2 points)

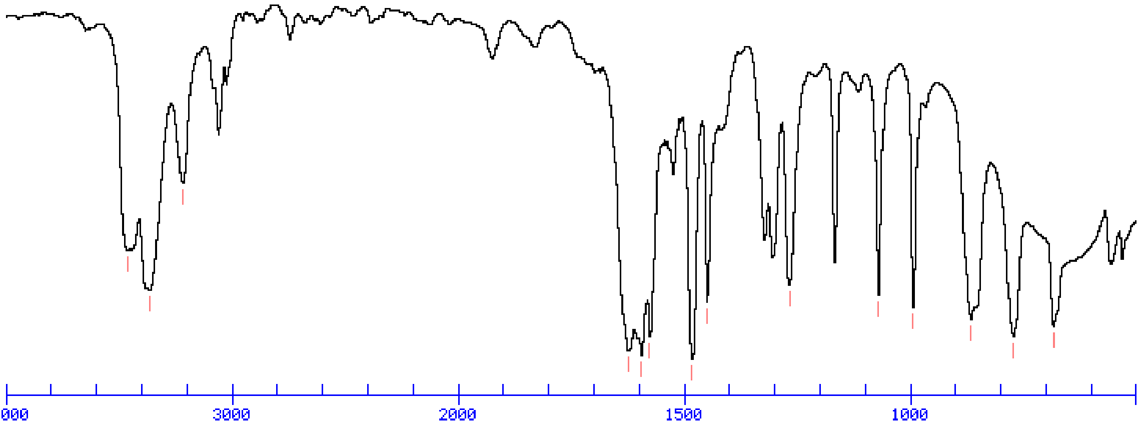
4. Explain why 3-Chloropentane shows four different absorbencies in the ^{1}H NMR spectrum. (3 points)



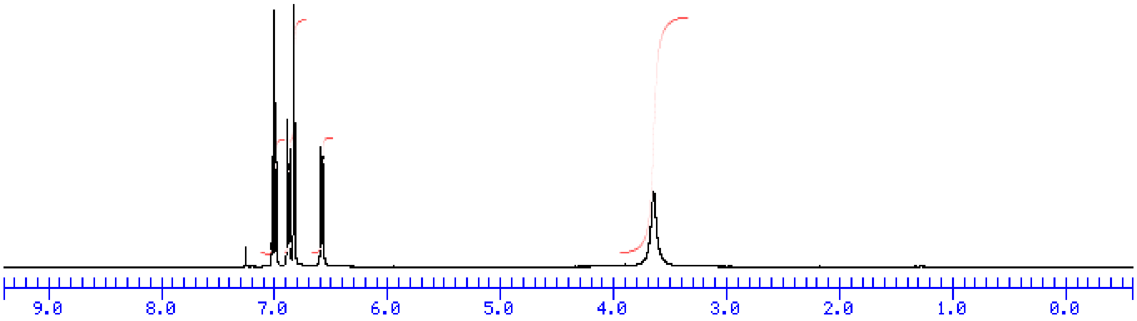
5. Write the structure from the data given. (4 points)

Molecular formula C_xH_yNBr

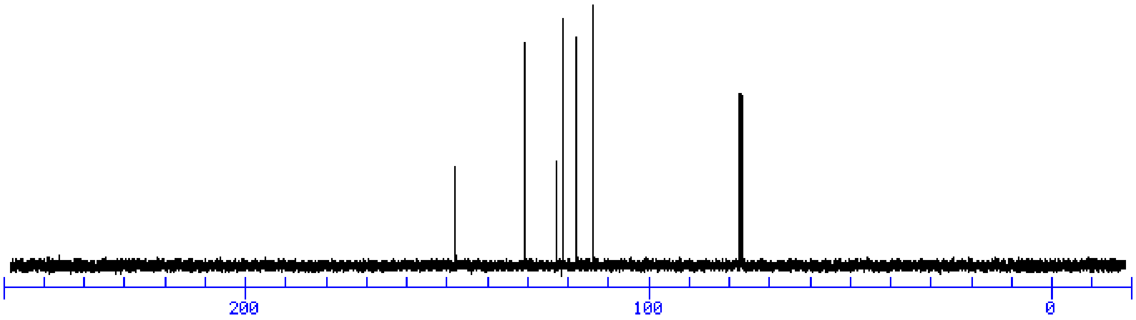
IR:



^{1}H NMR:



^{13}C NMR:



Report QuestionsNMR Laboratory

(Total 70 Points)

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………………………………………………………….. (signature)

Print Name: ____

1. Explain each of the following observations. (3 X 2= 6 points)

(a) The compound $CH_3CH_2CH = CH_2$ shows an IR absorbance around 1550 cm–1, but its structural isomer $CH_3CH = CHCH_3$ does not-why?

(b) The ^1H-decoupled ^{13}C NMR spectrum of CHF_3 shows a single peak that is split into a quartet.

2.

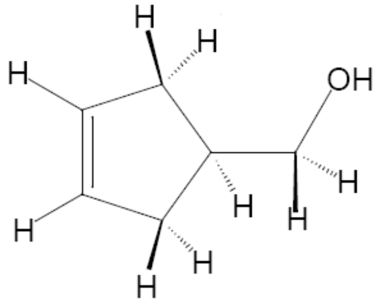
(a) Draw trans-4-(1-ethylpropyl)cyclohexanol in planar form (no chair). Be sure to indicate the stereochemistry. (2 points)

(b) Now draw trans-4-(1-ethylpropyl)cyclohexanol in its lowest energy conformation. (2 points)

(c) Now draw cis-4-(1-ethylpropyl)cyclohexanol in its lowest energy conformation. (2 points)

(d) Considering your answers to (b) and (c), which is lower in energy, cis or trans-4-(1-ethylpropyl)cyclohexanol? Explain your answer briefly (one sentence). (2 points)

3. In the following compound, label symmetry-equivalent H atoms with the same letter and nonequivalent H atoms with different letters, as we did in class. Then predict the ^1H NMR spectrum of the compound, indicating the approximate chemical shift, integration, and multiplicity for each resonance that you expect to see. (20 points)



Type of H	δ (in ppm)	Integration	Multiplicity

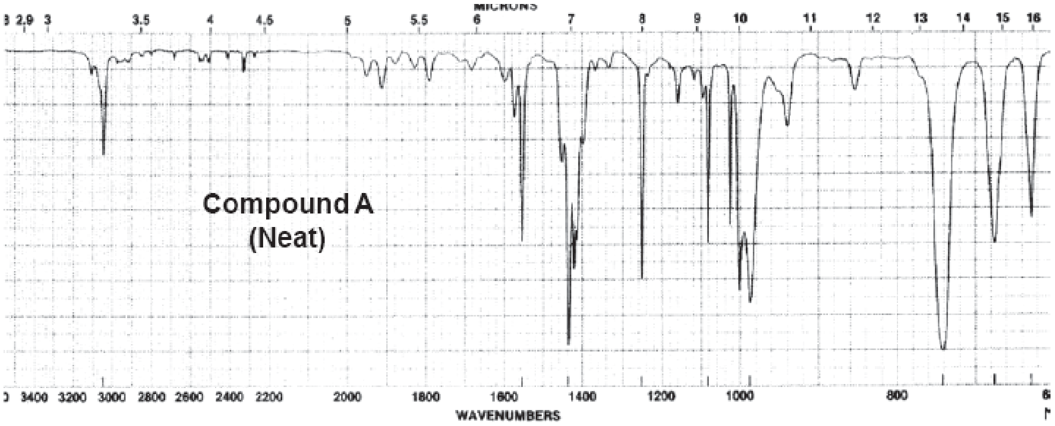
4. Below are the IR spectra of two isomers having the formula C_7H_7Cl. (Total 8 points)

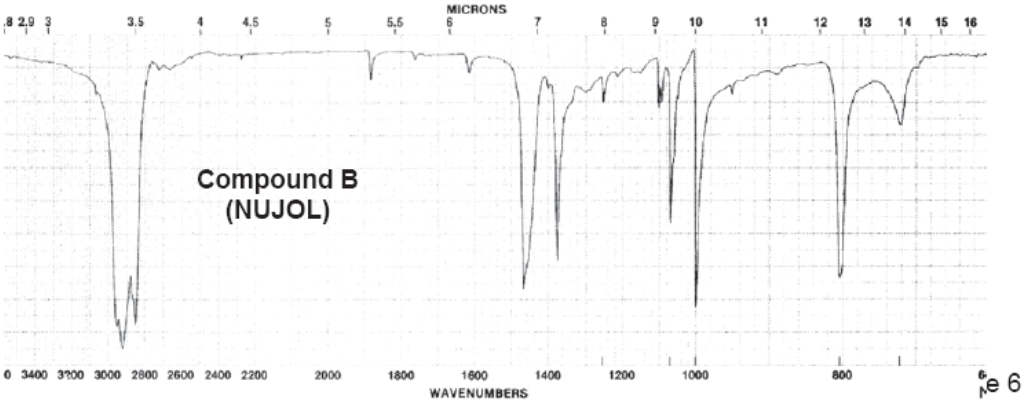
1) What is the unsaturation number of these isomers? _____ (2 points)

2) Why is there such a difference in the intensity of the C-H stretching and C-H bending region between these two isomeric compounds? (2 points)

3) What structure would you assign to Compound A? Indicate on the spectrum which IR bands support your structure assignment. (4 points)

4. What structure would you assign to Compound B? Indicate which IR bands support your structure assignment. Note: NUJOL is a paraffin oil used to prepared the IR sample. (8 points)

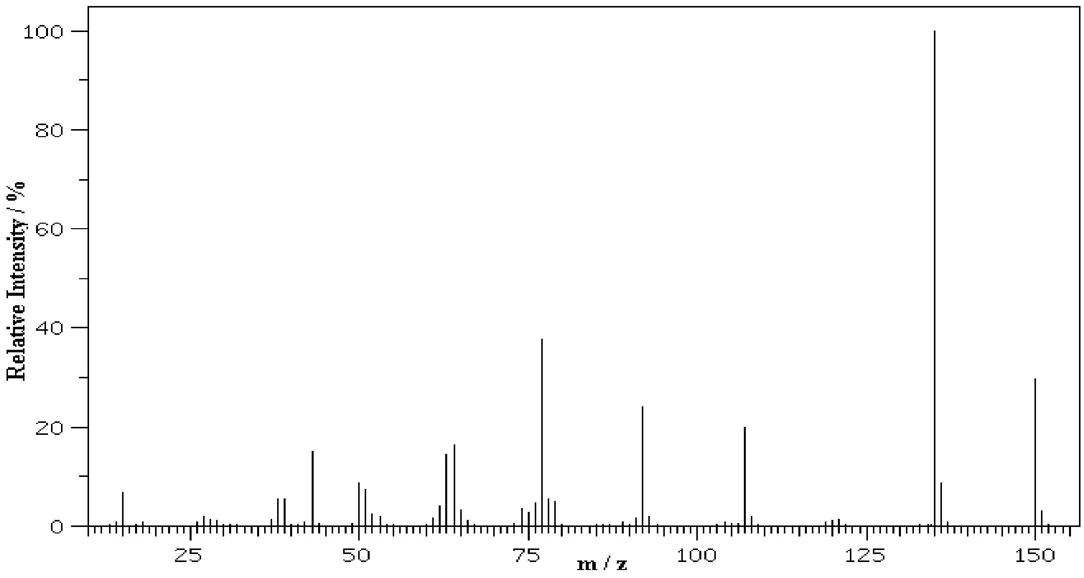




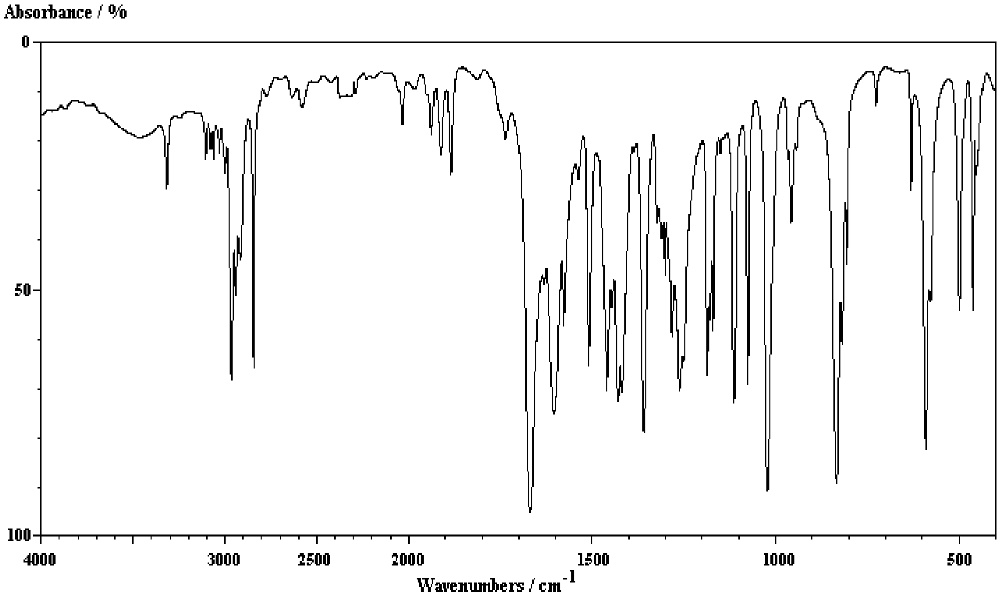
5. Find the structure of the compound and explain each spectrum to support your answer.

(a) Compound contains C, H, and O. (10 points)

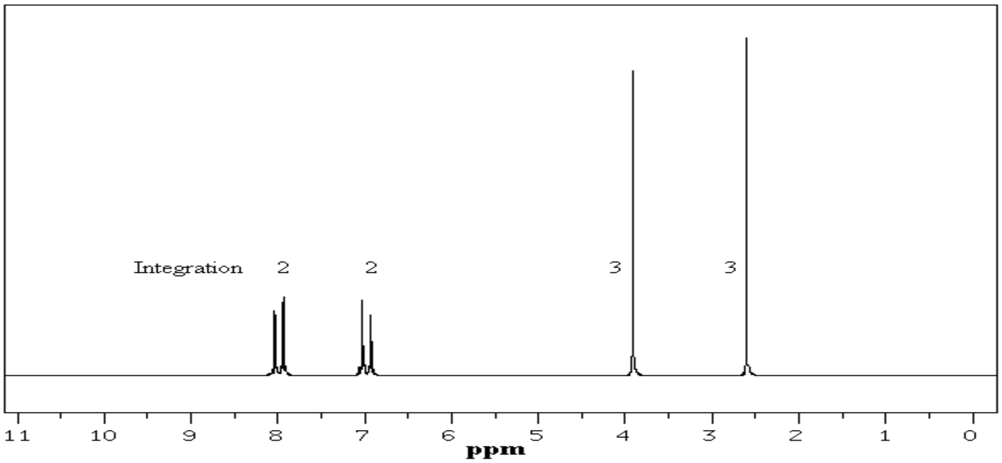
MS:


Relative Intensity / %
100
80
60
40
20
0
25
50
75
100
125
150
m / z

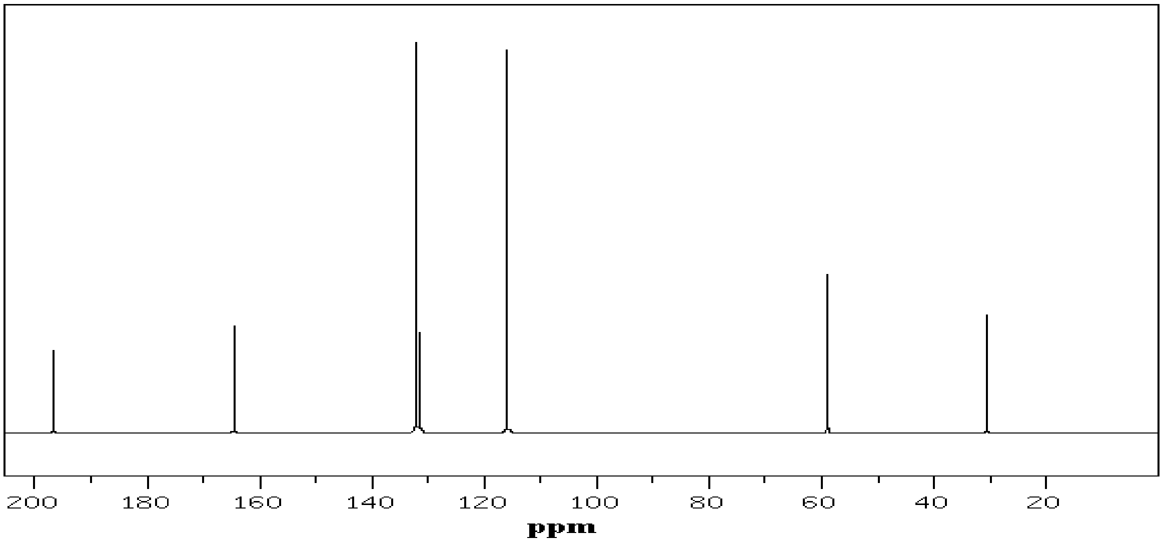
IR:


Absorbance / %
0
50
100
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm-1

^1H NMR:

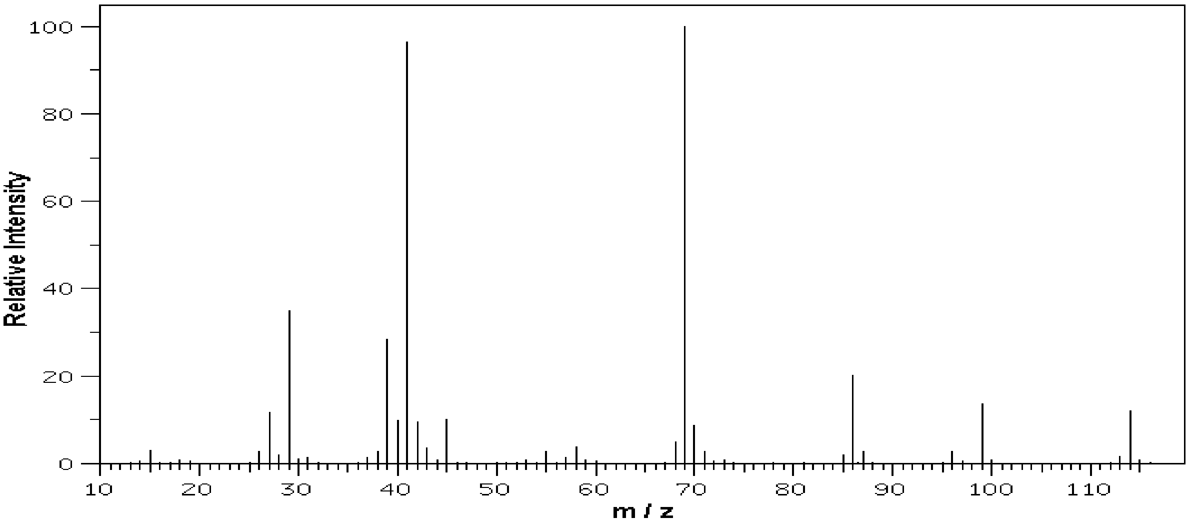


^{13}CNMR:

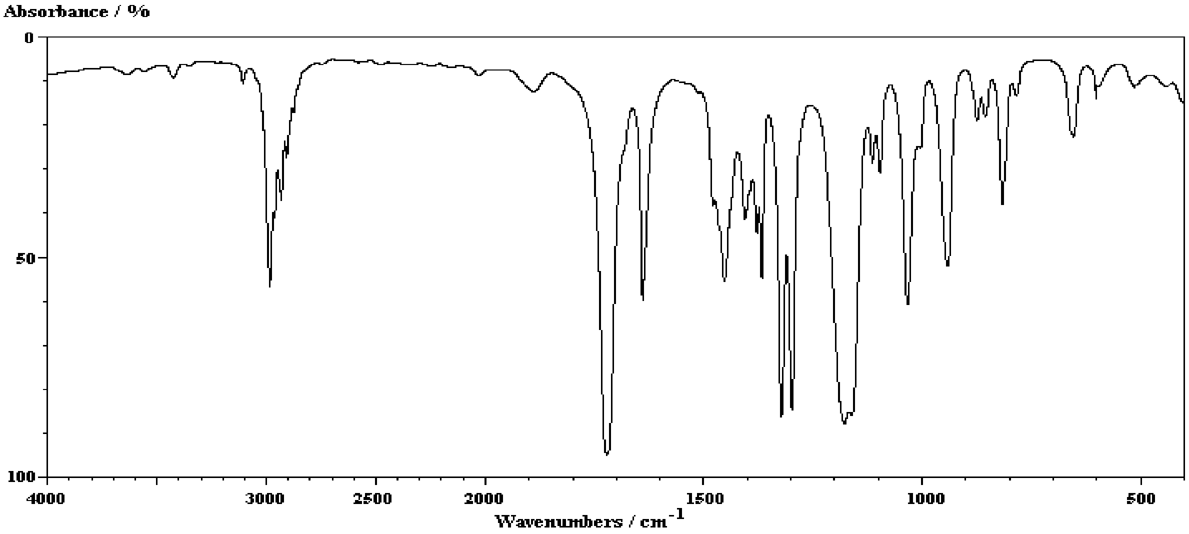


(b) Compound contains C, H, and O. (10 points)

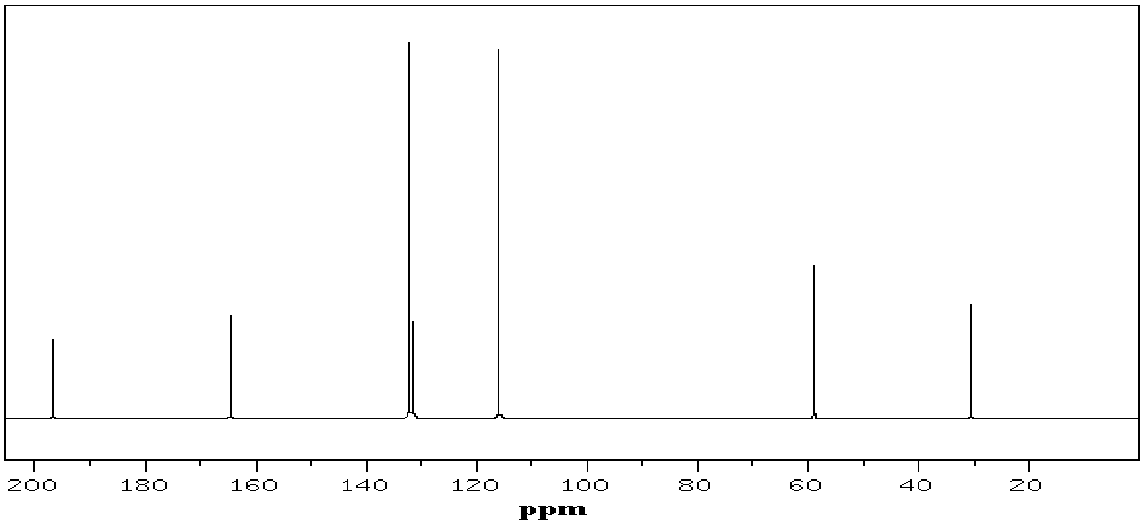
MS:


Relative Intensity
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
100
110
m / z

IR:

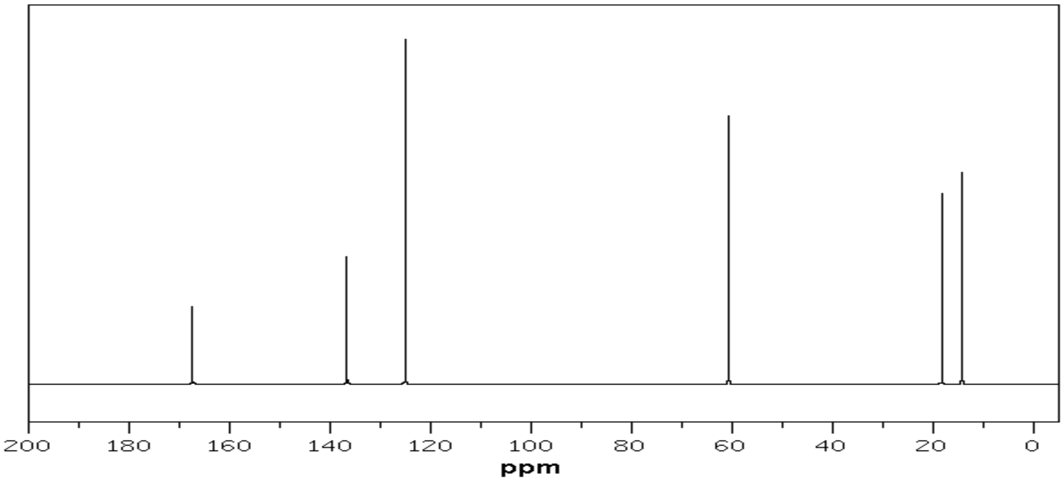

Absorbance / %
0
50
100
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm-1

^1H NMR:



200
180
160
140
120
100
80
60
40
20
ppm

^{13}C NMR:



200
180
160
140
120
100
80
60
40
20
0
ppm